Electronic Supplementary Information

Halogen-free pyrrolidinium bis(mandelato)borate ionic liquids: some physicochemical properties and lubrication performance as additives to polyethylene glycol

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N-pentyl-N-methylpyrrolidinium bis(mandelato)borate, [C_5C_1Pyrr][BMB]

The procedure is similar to that used for the synthesis of [C_4C_1Pyrr][BMB] described in 2.2.1. Bis(mandelato)borate sodium salt was synthesised in an aqueous solution of mandelic acid (15.21 g, 100 mmol), sodium carbonate (2.65 g, 25 mmol) and boric acid (3.09 g, 50 mmol) and mixed up with *N*-pentyl-*N*-methylpyrrolidinium bromide (11.81 g, 50 mmol), which was prepared from *N*-methylpyrrolidine and 1-bromopentane in toluene. An ionic liquid was obtained in 89 % yield (41.4 g).

Anal. Calcd. for $C_{26}H_{34}O_6BN$ (MW 467.06 g/mol) C, 66.81; H, 7.33; N, 2.99. Found: C, 65.3; H, 7.4; N, 3.1.

^{1}H NMR (359.92 MHz, $CDCl_3$): 7.65-7.56 (m, 4H, C_6H_5), 7.35-7.27 (m, 4H, C_6H_5), 7.26-7.23 (m, 2H, C_6H_5), 5.28 (d, 1H, $^4J_{HH}$ = 2.8 Hz, C_6H_5–C*H*), 5.24 (d, 1H, $^4J_{HH}$ = 4.2 Hz, C_6H_5–C*H*), 3.12-2.96 (m, 4H, N-(C*H*$_2$-CH$_2$-)$_2$, pyrrolidinium ring), 2.96-2.91 (m, 2H, N-C*H*$_2$-CH$_2$-, alkyl chain), 2.16 (s, 3H, N-C*H*$_3$), 1.89-1.87 (m, 4H, N-(CH$_2$-C*H*$_2$-)$_2$, pyrrolidinium ring), 1.48-1.39 (m, 2H, N-CH$_2$-C*H*$_2$-CH$_2$-, alkyl chain), 1.27-1.09 (m, 4H, (-C*H*$_2$-)$_2$, alkyl chain), 0.85 (t, 3H, $^3J_{HH}$ = 7.5 Hz, -CH$_2$-C*H*$_3$, alkyl chain) ppm.

^{13}C NMR (90.506 MHz, $CDCl_3$): 177.10 (s, 2C, >*C*=O), 140.04 (s, 2C, -*C*H(O)-), 129.09- 125.03 (12C, aromatic groups), 64.17 (t, 2C, $^1J_{CH}$ = 75.9 Hz, N-*C*H$_2$-, pyrrolidinium ring), 52.68 (t, 1C, $^1J_{CH}$ = 87.9 Hz, N-*C*H$_2$-, alkyl chain), 47.88 (q, 1C, $^1J_{CH}$ = 68.2 Hz, N-*C*H$_3$), 28.08-19.85 (5C methylene carbons of the pyrrolidinium ring and methylene carbons of the alkyl chain), 13.83 (q, 1C, $^1J_{CH}$ = 55.7 Hz, -*C*H$_3$, alkyl chain) ppm.

^{11}B NMR (115.48 MHz, $CDCl_3$): 11.06 ppm.

N-hexyl-N-methylpyrrolidinium bis(mandelato)borate, [C_6C_1Pyrr][BMB]

The procedure is similar to that used for the synthesis of [C_4C_1Pyrr][BMB] described in 2.2.1. Bis(mandelato)borate sodium salt was synthesised in an aqueous solution of mandelic acid (15.21 g, 100 mmol), sodium carbonate (2.65 g, 25 mmol) and boric acid (3.09 g, 50 mmol) and mixed up with *N*-hexyl-*N*-methylpyrrolidinium bromide (12.51 g, 50 mmol), which was prepared from *N*-methylpyrrolidine and 1-bromohexane in toluene. An ionic liquid was obtained in 87 % yield (41.9 g).

Anal. Calcd. for $C_{27}H_{36}O_6BN$ (MW 481.38 g/mol) C, 67.36; H, 7.53; N, 2.91. Found: C, 66.3; H, 7.6; N, 3.0.

^{1}H NMR (359.92 MHz, $CDCl_3$): 7.62-7.53 (m, 4H, C_6H_5), 7.32-7.31 (m, 4H, C_6H_5), 7.28-7.23 (m, 2H, C_6H_5), 5.27 (d, 1H, $^4J_{HH}$ = 3.1 Hz, C_6H_5–C*H*), 5.23 (d, 1H, $^4J_{HH}$ = 3.7 Hz, C_6H_5–C*H*), 3.05-2.99 (m, 4H, N-(C*H*$_2$-CH$_2$-)$_2$, pyrrolidinium ring), 2.89-2.85 (m, 2H, N-C*H*$_2$-CH$_2$-, alkyl chain), 2.54 (s,

3H, N-CH_3), 1.84-1.81 (m, 4H, N-(CH_2-CH_2-)$_2$, pyrrolidinium ring), 1.42-1.40 (m, 2H, N-CH_2-CH_2-CH_2-, alkyl chain), 1.26-1.10 (m, 6H, (-CH_2-)$_3$, alkyl chain), 0.85 (t, 3H, $^3J_{HH}$ = 7.4 Hz, CH_2-CH_3, alkyl chain) ppm.

^{13}C NMR (90.506 MHz, $CDCl_3$): 177.71 (s, 2C, >*C*=O), 140.10 (s, 2C, -*C*H(O)-), 129.19-125.30 (12C, aromatic groups), 64.08 (t, 2C, $^1J_{CH}$ = 77.2 Hz, N-*C*H_2-, pyrrolidinium ring), 53.71 (t, 1C, $^1J_{CH}$ = 86.8 Hz, N-*C*H_2-, alkyl chain), 47.80 (q, 1C, $^1J_{CH}$ = 67.7 Hz, N-*C*H_3), 32.44-19.69 (6C methylene carbons of the pyrrolidinium ring and methylene carbons of the alkyl chain), 13.90 (q, 1C, $^1J_{CH}$ = 56.1 Hz, -*C*H_3, alkyl chain) ppm.

^{11}B NMR (115.48 MHz, $CDCl_3$): 11.09 ppm.

N-heptyl-N-methylpyrrolidinium bis(mandelato)borate, [C_7C_1Pyrr][BMB]

The procedure is similar to that used for the synthesis of [C_4C_1Pyrr][BMB] described in 2.2.1. Bis(mandelato)borate sodium salt was synthesised in an aqueous solution of mandelic acid (15.21 g, 100 mmol), sodium carbonate (2.65 g, 25 mmol) and boric acid (3.09 g, 50 mmol) and mixed up with *N*-heptyl-*N*-methylpyrrolidinium bromide (13.21 g, 50 mmol), which was prepared from *N*-methylpyrrolidine and 1-bromoheptane in toluene. An ionic liquid was obtained in 87 % yield (42.9 g).

Anal. Calcd. for $C_{28}H_{38}O_6BN$ (MW 495.41 g/mol) C, 67.88; H, 7.74; N, 2.82. Found: C, 67.1; H, 7.8; N, 3.0.

^{1}H NMR (359.92 MHz, $CDCl_3$): 7.64-7.53 (m, 4H, C_6H_5), 7.31-7.39 (m, 4H, C_6H_5), 7.28-7.24 (m, 2H, C_6H_5), 5.28 (d, 1H, $^4J_{HH}$ = 3.8 Hz, C_6H_5–C*H*), 5.24 (d, 1H, $^4J_{HH}$ = 4.7 Hz, C_6H_5–C*H*), 3.04-2.90 (m, 4H, N-(CH_2-CH_2-)$_2$, pyrrolidinium ring), 2.89-2.85 (m, 2H, N-CH_2-CH_2-, alkyl chain), 2.55 (s, 3H, N-CH_3), 1.85-1.81 (m, 4H, N-(CH_2-CH_2-)$_2$, pyrrolidinium ring), 1.44-1.41 (m, 2H, N-CH_2-CH_2-CH_2-, alkyl chain), 1.38-1.07 (m, 8H, (-CH_2-)$_4$, alkyl chain), 0.87 (t, 3H, $^3J_{HH}$ = 7.5 Hz, -CH_2-CH_3, alkyl chain) ppm.

^{13}C NMR (90.506 MHz, $CDCl_3$): 177.92 (s, 2C, >*C*=O), 140.07 (s, 2C, -*C*H(O)-), 129.13-125.31 (12C, aromatic groups), 64.11 (t, 2C, $^1J_{CH}$ = 77.2 Hz, N-*C*H_2-, pyrrolidinium ring), 53.55 (t, 1C, $^1J_{CH}$ = 88.1 Hz, N-*C*H_2-, alkyl chain), 47.86 (q, 1C, $^1J_{CH}$ = 66.5 Hz, N-*C*H_3), 32.84-19.76 (7C methylene carbons of the pyrrolidinium ring and methylene carbons of the alkyl chain), 13.96 (q, 1C, $^1J_{CH}$ = 54.1 Hz, -*C*H_3, alkyl chain) ppm.

^{11}B NMR (115.48 MHz, $CDCl_3$): 11.09 ppm.

N-octyl-N-methylpyrrolidinium bis(mandelato)borate, [C_8C_1Pyrr][BMB]

The procedure is similar to that used for the synthesis of [C_4C_1Pyrr][BMB] described in 2.2.1. Bis(mandelato)borate sodium salt was synthesised in an aqueous solution of mandelic acid (15.21 g, 100 mmol), sodium carbonate (2.65 g, 25 mmol) and boric acid (3.09 g, 50 mmol) and mixed up with *N*-octyl-*N*-methylpyrrolidinium chloride (11.69 g, 50 mmol), which was prepared from *N*-methylpyrrolidine and 1-chloroctane in toluene. An ionic liquid was obtained in 70 % yield (35.7 g).

Anal. Calcd. for $C_{29}H_{40}O_6BN$ (MW 509.44 g/mol) C, 68.37; H, 7.91; N, 2.75. Found: C, 67.9; H, 8.0; N, 2.9.

^{1}H NMR (359.92 MHz, $CDCl_3$): 7.63-7.54 (m, 4H, C_6H_5), 7.34-7.30 (m, 4H, C_6H_5), 7.29-7.25 (m, 2H, C_6H_5), 5.29 (d, 1H, $^4J_{HH}$ = 6.3 Hz, C_6H_5–C*H*), 5.25 (d, 1H, $^4J_{HH}$ = 5.4 Hz, C_6H_5–C*H*), 3.10-2.91 (m, 4H, N-(CH_2-CH_2-)$_2$, pyrrolidinium ring), 2.88-2.84 (m, 2H, N-CH_2-CH_2-, alkyl chain), 2.58 (s, 3H, N-CH_3), 1.89-1.84 (m, 4H, N-(CH_2-CH_2-)$_2$, pyrrolidinium ring), 1.47-1.40 (m, 2H, N-CH_2-CH_2-CH_2-, alkyl chain), 1.37-1.12 (m, 10H, (-CH_2-)$_5$, alkyl chain), 0.89 (t, 3H, $^3J_{HH}$ = 8.4 Hz, -CH_2-CH_3, alkyl chain) ppm.

^{13}C NMR (90.506 MHz, $CDCl_3$): 178.23 (s, 2C, >*C*=O), 140.02 (s, 2C, -*C*H(O)-), 129.18-125.23 (12C, aromatic groups), 64.31 (t, 2C, $^1J_{CH}$ = 77.19 Hz, N-*C*H_2-, pyrrolidinium ring), 48.04 (q, 1C, $^1J_{CH}$ = 67.2 Hz, N-*C*H_3), 33.02-19.77 (8C, methylene carbons of the pyrrolidinium ring and methylene carbons of the alkyl chain), 14.06 (q, 1C, $^1J_{CH}$ = 56.4 Hz, -*C*H_3, alkyl chain) ppm.

^{11}B NMR (115.48 MHz, $CDCl_3$): 11.09 ppm.

N-decyl-N-methylpyrrolidinium bis(mandelato)borate, [$C_{10}C_1$Pyrr][BMB]

The procedure is similar to that used for the synthesis of [C_4C_1Pyrr][BMB] described in 2.2.1. Bis(mandelato)borate sodium salt was synthesised in an aqueous solution of with mandelic acid (15.21 g, 100 mmol), sodium carbonate (2.65 g, 25 mmol) and boric acid (3.09 g, 50 mmol) and mixed up with *N*-decyl-*N*-methylpyrrolidinium bromide (15.32 g, 50 mmol), which was prepared from *N*-methylpyrrolidine and 1-bromodecane in toluene. An ionic liquid was obtained in 84 % yield (44.9 g).

Anal. Calcd. for $C_{31}H_{44}O_6BN$ (MW 537.49 g/mol) C, 69.71; H, 8.25; N, 2.60. Found: C, 68.4; H, 8.25; N, 2.75.

^{1}H NMR (359.92 MHz, $CDCl_3$): 7.63-7.53 (m, 4H, C_6H_5), 7.34-7.39 (m, 4H, C_6H_5), 7.29-7.22 (m, 2H, C_6H_5), 5.28 (d, 1H, $^4J_{HH}$ = 2.8 Hz, C_6H_5–C*H*), 5.24 (d, 1H, $^4J_{HH}$ = 4.6 Hz, C_6H_5–C*H*), 3.04-2.90 (m, 4H, N-(CH_2-CH_2-)$_2$, pyrrolidinium ring), 2.88-2.85 (m, 2H, N-CH_2-CH_2-, alkyl chain), 2.55 (s, 3H, N-CH_3), 1.84-1.81 (m, 4H, N-(CH_2-CH_2-)$_2$, pyrrolidinium ring), 1.41-1.39 (m, 2H, N-CH_2-CH_2-CH_2-, alkyl chain), 1.38-1.07 (m, 14H, (-CH_2-)$_7$, alkyl chain), 0.89 (t, 3H, $^3J_{HH}$ = 7.5 Hz, -CH_2-CH_3, alkyl chain) ppm.

^{13}C NMR (90.506 MHz, $CDCl_3$): 177.91 (s, 2C, >*C*=O), 139.99 (s, 2C, -*C*H(O)-), 129.07-125.40 (12C, aromatic groups), 64.04 (t, 2C, $^1J_{CH}$ = 77.2 Hz, N-*C*H_2-, pyrrolidinium ring), 47.81 (q, 1C, $^1J_{CH}$ = 65.1 Hz, N-*C*H_3), 33.25-19.67 (10C, methylene carbons of the pyrrolidinium ring and methylene carbons of the alkyl chain), 14.12 (q, 1C, $^1J_{CH}$ = 55.3 Hz, -*C*H_3, alkyl chain) ppm.

^{11}B NMR (115.48 MHz, $CDCl_3$): 11.08 ppm.

N-dodecyl-N-methylpyrrolidinium bis(mandelato)borate, [$C_{12}C_1$Pyrr][BMB]

The procedure is similar to that used for the synthesis of [C_4C_1Pyrr][BMB] described in 2.2.1. Bis(mandelato)borate sodium salt was synthesised in an aqueous solution of mandelic acid (15.21 g, 100 mmol), sodium carbonate (2.65 g, 25 mmol) and boric acid (3.09 g, 50 mmol) and mixed up with *N*-dodecyl-*N*-methylpyrrolidinium chloride (14.49 g, 50 mmol), which was prepared from *N*-methylpyrrolidine and 1-chlorododecane in toluene. An ionic liquid was obtained in 68 % yield (38.7 g).

Anal. Calcd. for $C_{33}H_{48}O_6BN$ (MW 565.54 g/mol) C, 70.08; H, 8.55; N, 2.47. Found: C, 69.1; H, 8.9; N, 2.6.

^{1}H NMR (359.92 MHz, $CDCl_3$): 7.63-7.54 (m, 4H, C_6H_5), 7.34-7.30 (m, 4H, C_6H_5), 7.29-7.22 (m, 2H, C_6H_5), 5.29 (d, 1H, $^4J_{HH}$ = 4.2 Hz, C_6H_5–C*H*), 5.25 (d, 1H, $^4J_{HH}$ = 5.9 Hz, C_6H_5–C*H*), 3.10-3.05 (m, 4H, N-(CH_2-CH_2-)$_2$, pyrrolidinium ring), 2.87-2.84 (m, 2H, N-CH_2-CH_2-, alkyl chain), 2.58 (s, 3H, N-*C*H_3), 1.88-1.83 (m, 4H, N-(CH_2-CH_2-)$_2$, pyrrolidinium ring), 1.44-1.34 (m, 2H, N-CH_2-CH_2-CH_2-, alkyl chain), 1.26-1.09 (m, 18H, (-CH_2-)$_9$, alkyl chain), 0.88 (t, 3H, $^3J_{HH}$ = 7.5 Hz, -CH_2-CH_3, alkyl chain) ppm.

^{13}C NMR (90.506 MHz, $CDCl_3$): 177.98 (s, 2C, >*C*=O), 140.03 (s, 2C, -*C*H(O)-), 127.36-125.39 (12C, aromatic groups), 64.18 (t, 2C, $^1J_{CH}$ = 76.3 Hz, N-*C*H_2-, pyrrolidinium ring), 47.92 (q, 1C, $^1J_{CH}$ = 68.3 Hz, N-*C*H_3), 32.45-19.77 (12C, methylene carbons of the pyrrolidinium ring and methylene carbons of the alkyl chain), 16.23 (q, 1C, $^1J_{CH}$ = 56.4 Hz, -*C*H_3, alkyl chain) ppm.

^{11}B NMR (115.48 MHz, $CDCl_3$): 10.97 ppm.

N-tetradecyl-N-methylpyrrolidinium bis(mandelato)borate, [$C_{14}C_1$Pyrr][BMB]

The procedure is similar to that used for the synthesis of [C_4C_1Pyrr][BMB] described in 2.2.1. Bis(mandelato)borate sodium salt was synthesised in an aqueous solution of mandelic acid (15.21 g, 100 mmol), sodium carbonate (2.65 g, 25 mmol) and boric acid (3.09 g, 50 mmol) and mixed up with *N*-tetradecyl-*N*-methylpyrrolidinium bromide (18.12 g, 50 mmol), which was prepared from *N*-methylpyrrolidine and 1-bromotetradecane in toluene. An ionic liquid was obtained in 72 % yield (42.9 g).

Anal. Calcd. for $C_{35}H_{52}O_6BN$ (MW 593.60 g/mol) C, 70.81; H, 8.83; N, 2.36. Found: C, 69.4; H, 9.05; N, 2.35.

^{1}H NMR (359.92 MHz, $CDCl_3$): 7.65-7.57 (m, 4H, C_6H_5), 7.36-7.30 (m, 4H, C_6H_5), 7.27-7.21 (m, 2H, C_6H_5), 5.33 (d, 1H, $^{4}J_{HH}$ = 6.3 Hz, C_6H_5–C*H*), 5.26 (d, 1H, $^{4}J_{HH}$ = 5.7 Hz, C_6H_5–C*H*), 3.11-3.10 (m, 4H, N-(C*H*$_2$-CH$_2$-)$_2$, pyrrolidinium ring), 2.86-2.82 (m, 2H, N-C*H*$_2$-CH$_2$-, alkyl chain), 2.35 (s, 3H, N-C*H*$_3$), 1.92-1.81 (N-(CH$_2$-C*H*$_2$-)$_2$, pyrrolidinium ring), 1.48-1.39 (m, 2H, N-CH$_2$-C*H*$_2$-CH$_2$-, alkyl chain), 1.26-1.20 (m, 22H, (-C*H*$_2$-)$_{11}$, alkyl chain), 0.88 (t, 3H, $^{3}J_{HH}$ = 7.5 Hz, -CH$_2$-C*H*$_3$, alkyl chain) ppm.

^{13}C NMR (90.506 MHz, $CDCl_3$): 178.22 (s, 2C, >*C*=O), 140.19 (s, 2C, -*C*H(O)-), 127.44-125.50 (12C, aromatic groups), 64.38 (t, 2C, $^{1}J_{CH}$ = 77.3 Hz, N-*C*H$_2$-, pyrrolidinium ring), 48.19 (q, 1C, $^{1}J_{CH}$ = 67.5 Hz, N-*C*H$_3$), 29.68-19.95 (14C, methylene carbons of the pyrrolidinium ring and methylene carbons of the alkyl chain), 16.32 (q, 1C, $^{1}J_{CH}$ = 57.3 Hz, -*C*H$_3$, alkyl chain) ppm.

^{11}B NMR (115.48 MHz, $CDCl_3$): 10.90 ppm.

Elemental Analysis

The elemental analysis for carbon, hydrogen and nitrogen (CHN) was performed according to the Dumas method using Flash EA 1112 from Thermo Finnigan elemental analyser. About 1 mg of the sample was weighed in a tin capsule, sealed and placed in an auto sampler, from which it was dropped into a combustion chamber. As the sample entered the combustion chamber oxygen was injected into the carrier gas (He), which flowed through the combustion tube. The temperature was raised to 1800 °C, which insured the complete combustion of the sample. Detection was made with a Hot Wire Detector (HWD). The quantification was made using certified external standards and the method of least squares with the correlation coefficient > 0.999.[1]

Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS)

For sodium, chlorine and bromine elemental analysis, approximately 20 mg of sample was digested with 1 mL concentrated HNO_3 (MW-assisted digestion in closed Teflon vessels). After cooling to room temperature the digest was diluted with MQ water. Concentrations of the elements were determined by the ICP-SFMS using a combination of internal standardization and external calibration. Elemental analysis was carried out in the medium resolution range, Δm/m = 4500 (Finnigan MAT, Bremen, Germany).[2]

Karl Fischer Titration

831 Karl Fischer coulometer titration was used to determine water content in hf-BILs. HYDRANAL-COULOMAT AG (Fluka) was used as a reagent. Using an analytical balance about 100 mg of hf-BIL was measured and added to the titration vessel. Duplicate measurements were performed and the mean values and SD are calculated and tabulated in Table SI-1.

^{1}H, ^{13}C, ^{11}B NMR spectra of [C_nC_1Pyrr][BMB] ILs, *n* = 4, 5, 6, 7, 8, 10, 12 and 14

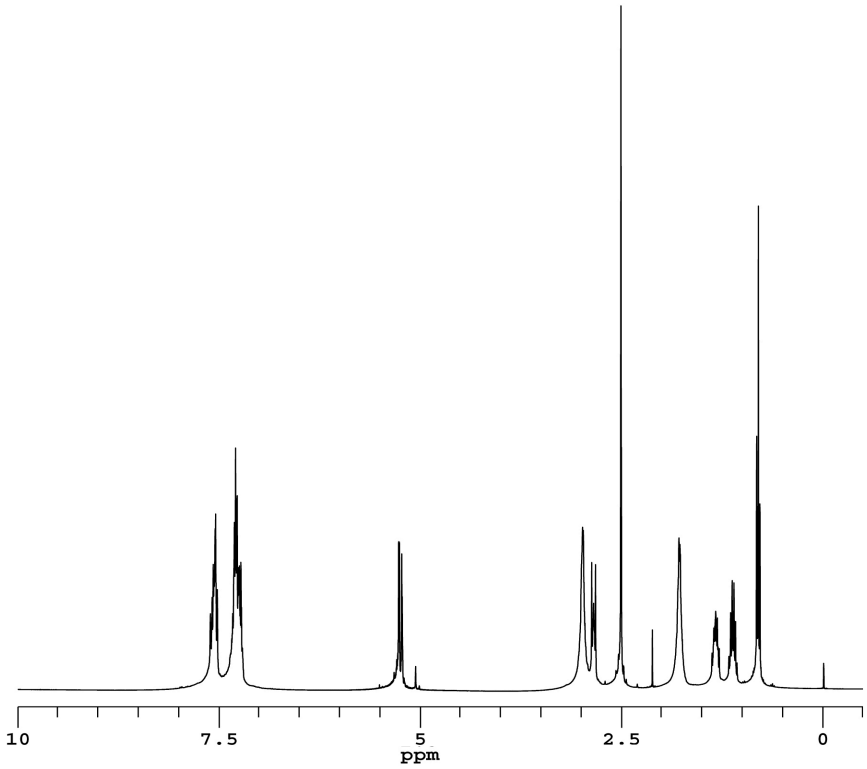

Figure SI-1. 359.92 MHz ^{1}H NMR spectrum of [C_4C_1Pyrr][BMB] in $CDCl_3$.

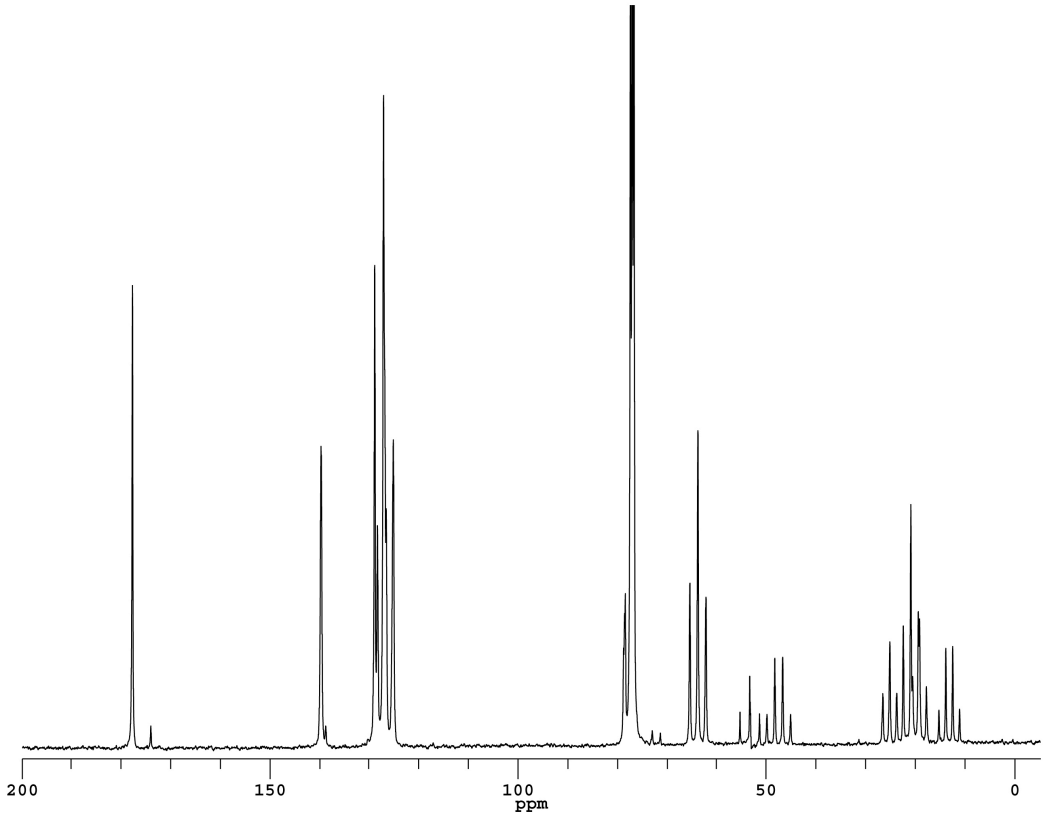

Figure SI-2. 90.506 MHz ^{13}C NMR spectrum of [C_4C_1Pyrr][BMB] in $CDCl_3$.

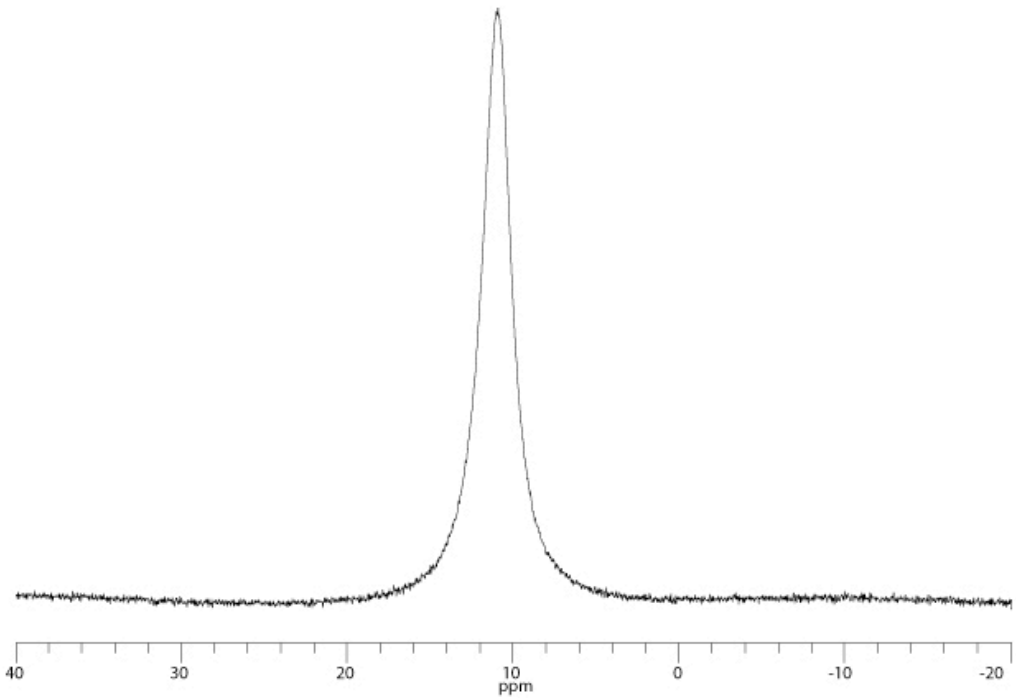

Figure SI-3. 115.48 MHz ^{11}B NMR spectrum of $[C_4C_1Pyrr][BMB]$ in $CDCl_3$.

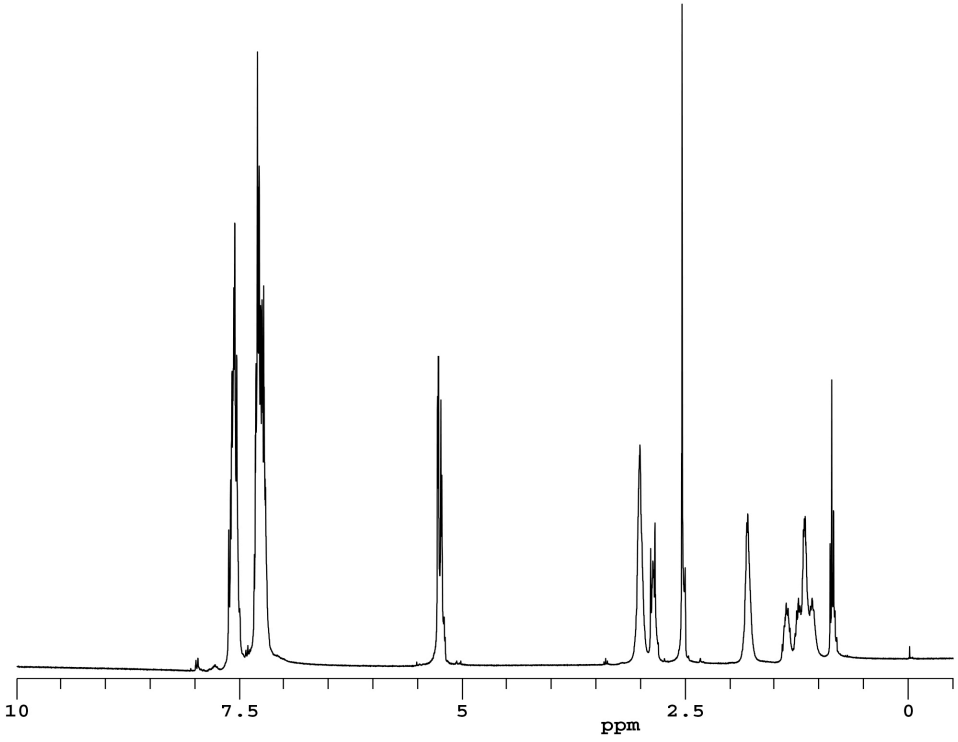

Figure SI-4. 359.92 MHz ^{1}H NMR spectrum of $[C_5C_1Pyrr][BMB]$ in $CDCl_3$.

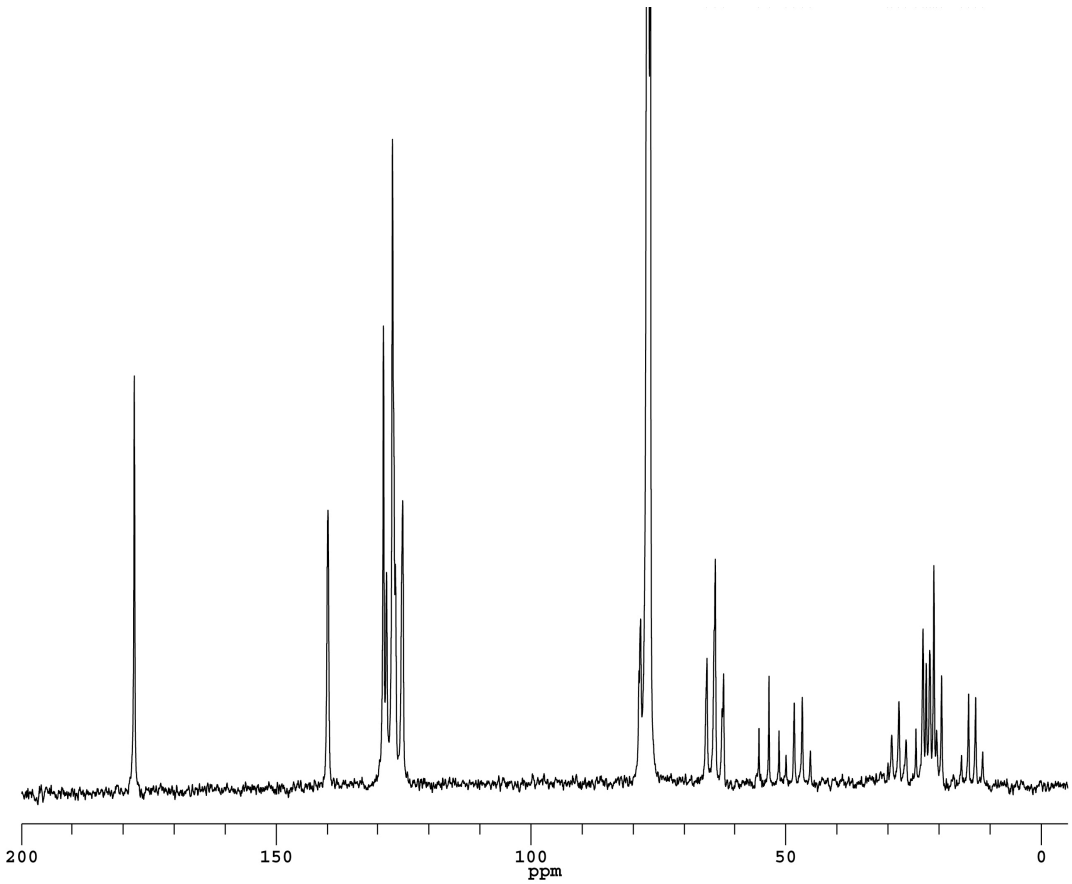

Figure SI-5. 90.506 MHz ^{13}C NMR spectrum of $[C_5C_1Pyrr][BMB]$ in $CDCl_3$.

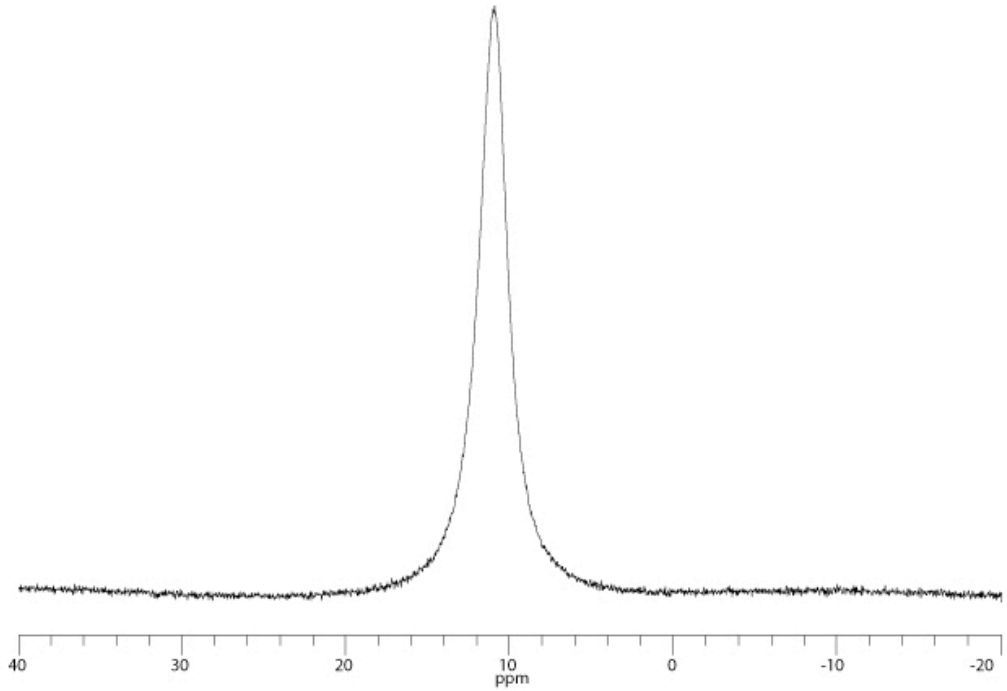

Figure SI-6. 115.48 MHz ^{11}B NMR spectrum of $[C_5C_1Pyrr][BMB]$ in $CDCl_3$.

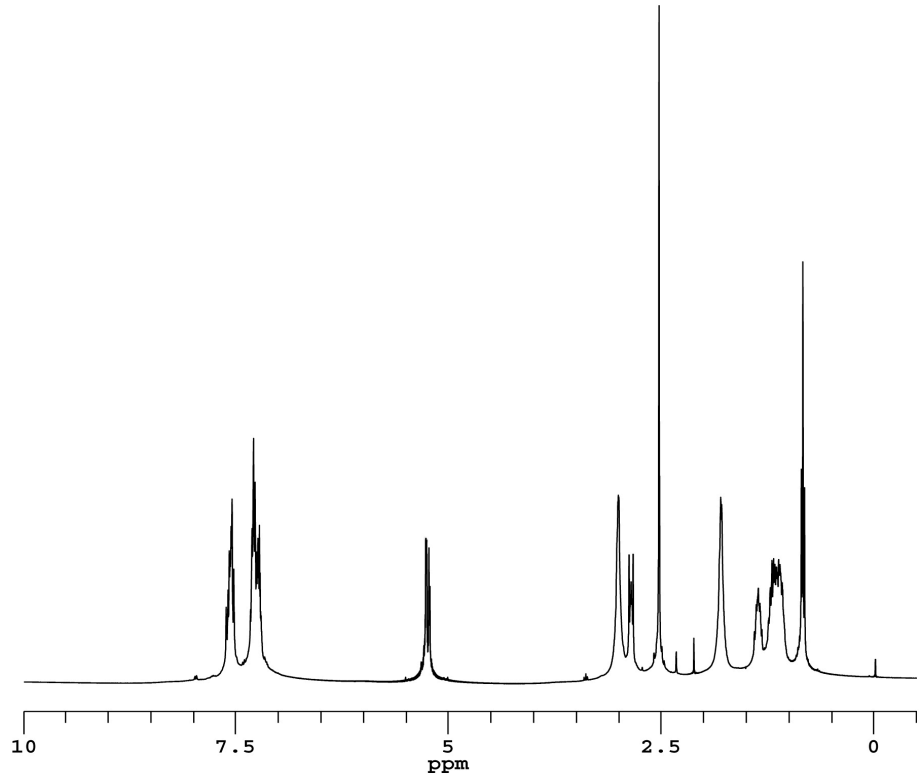

Figure SI-7. 359.92 MHz ^{1}H NMR spectrum of $[C_6C_1Pyrr][BMB]$ in $CDCl_3$.

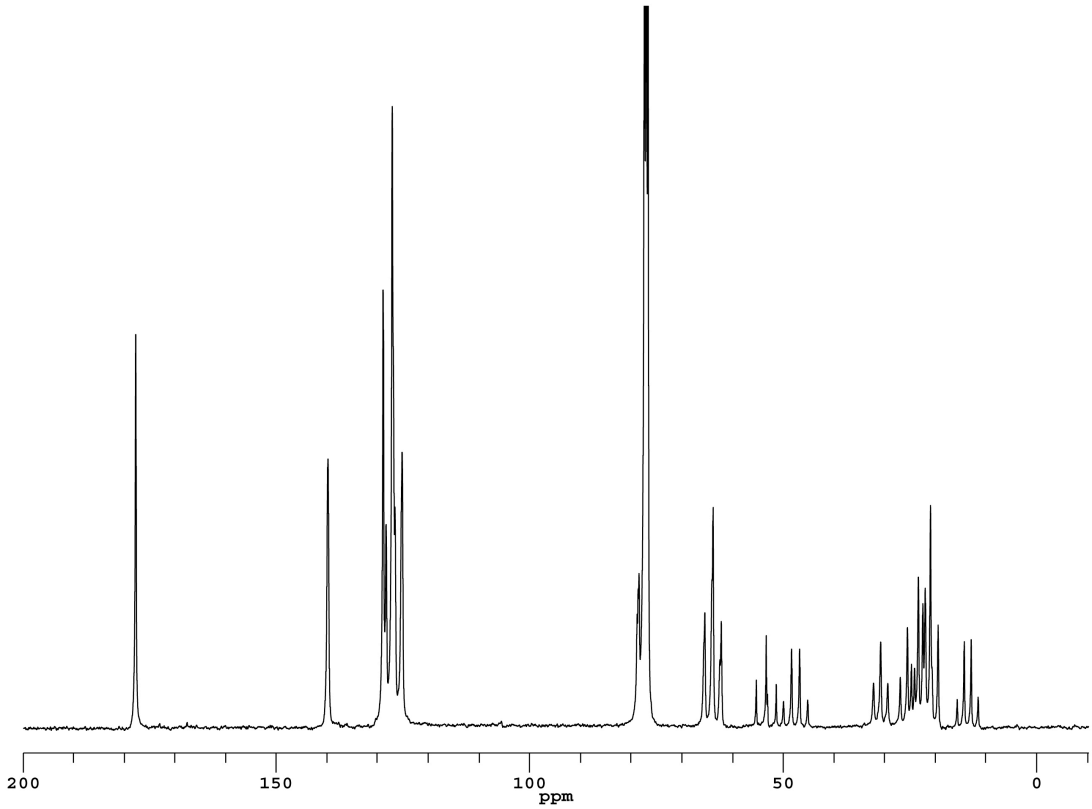

Figure SI-8. 90.506 MHz ^{13}C NMR spectrum of $[C_6C_1Pyrr][BMB]$ in $CDCl_3$.

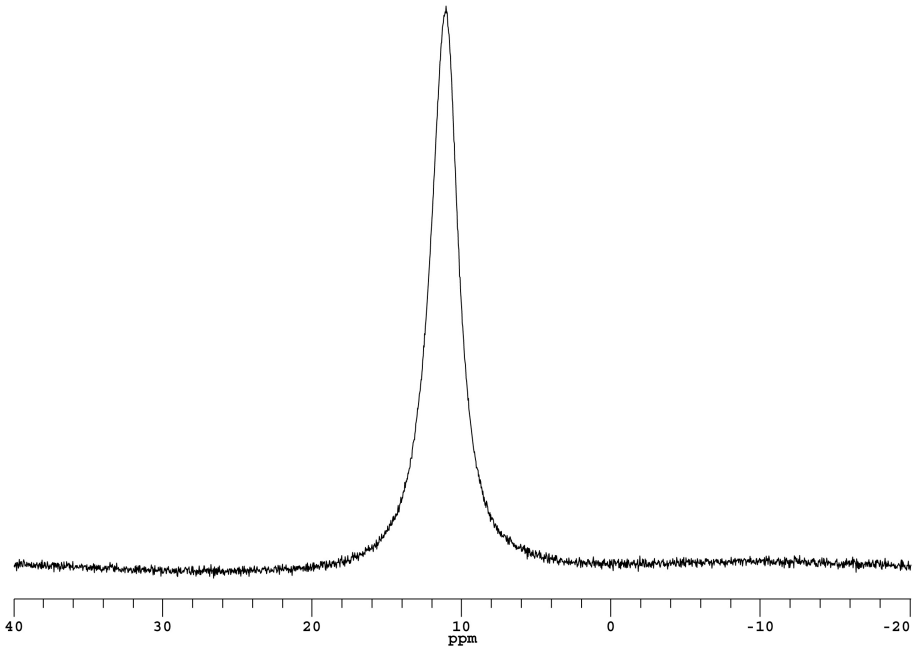

Figure SI-9. 115.48 MHz ^{11}B NMR spectrum of $[C_6C_1Pyrr][BMB]$ in $CDCl_3$.

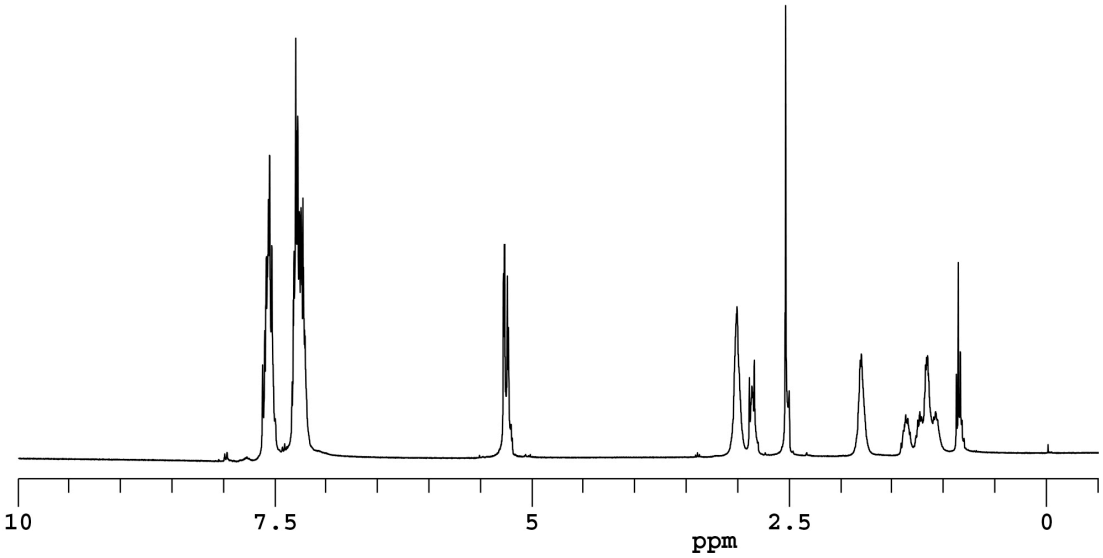

Figure SI-10. 359.92 MHz ^{1}H NMR spectrum of $[C_7C_1Pyrr][BMB]$ in $CDCl_3$.

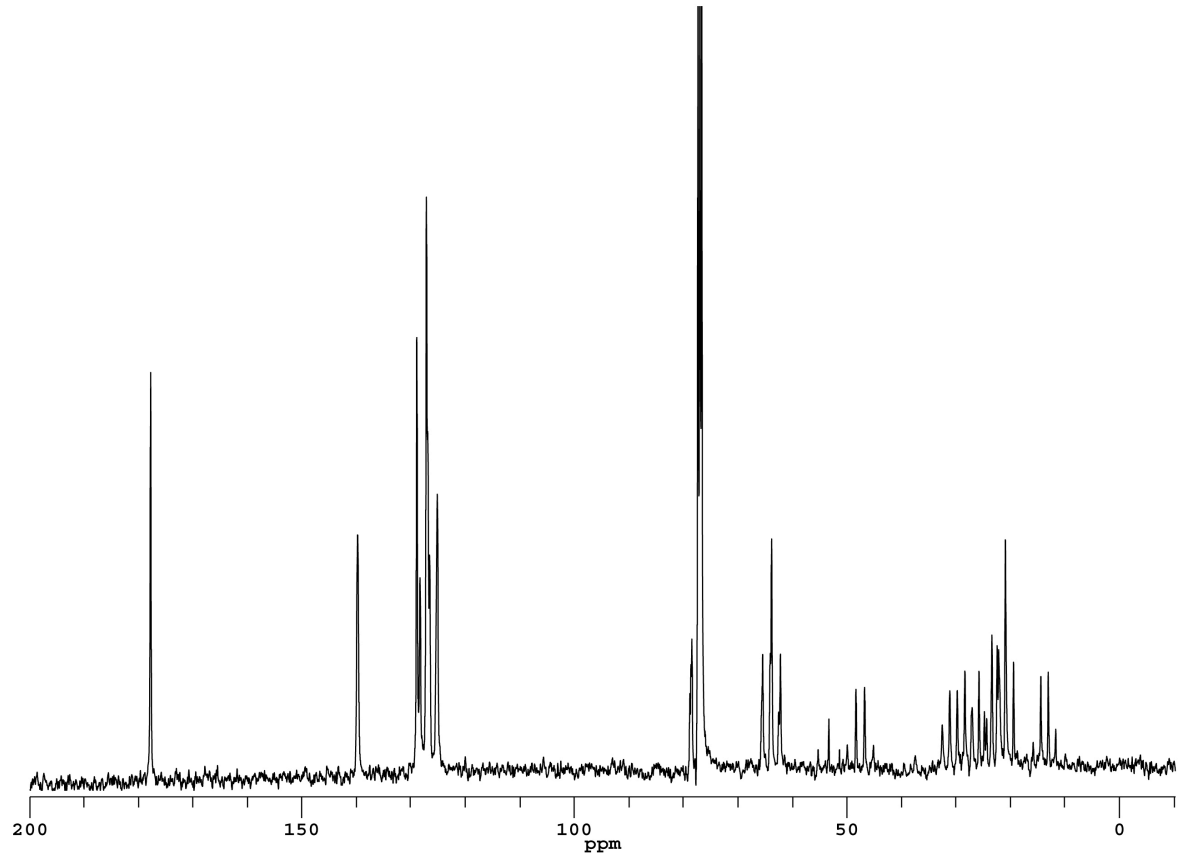

Figure SI-11. 90.506 MHz ^{13}C NMR spectrum of $[C_7C_1Pyrr][BMB]$ in $CDCl_3$.

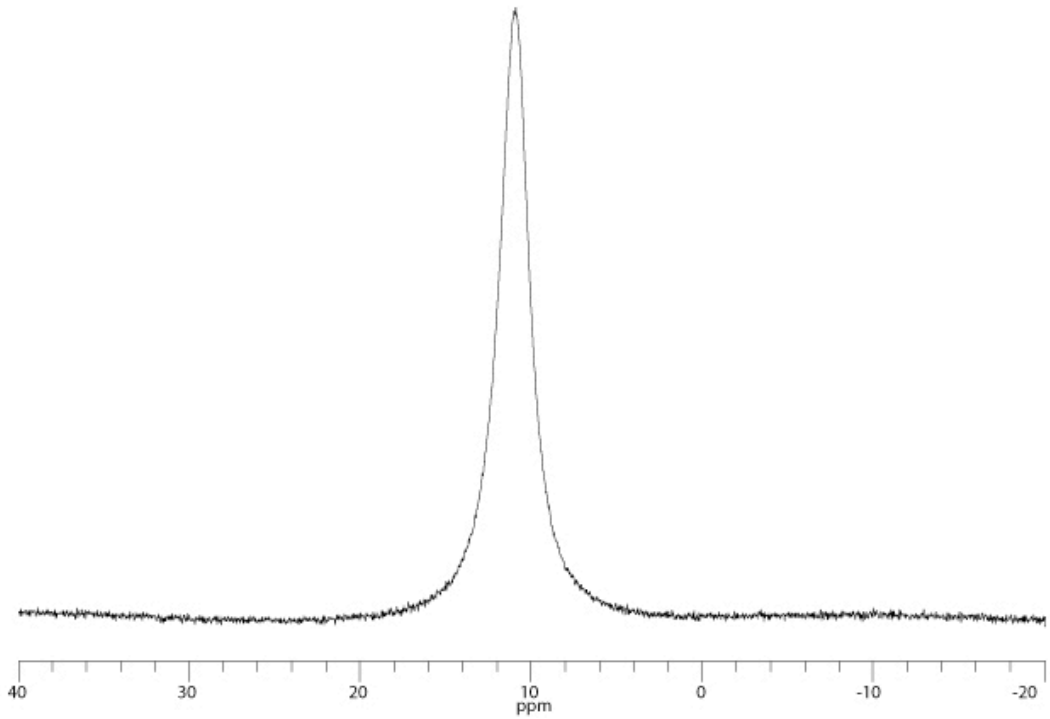

Figure SI-12. 115.48 MHz ^{11}B NMR spectrum of $[C_7C_1Pyrr][BMB]$ in $CDCl_3$.

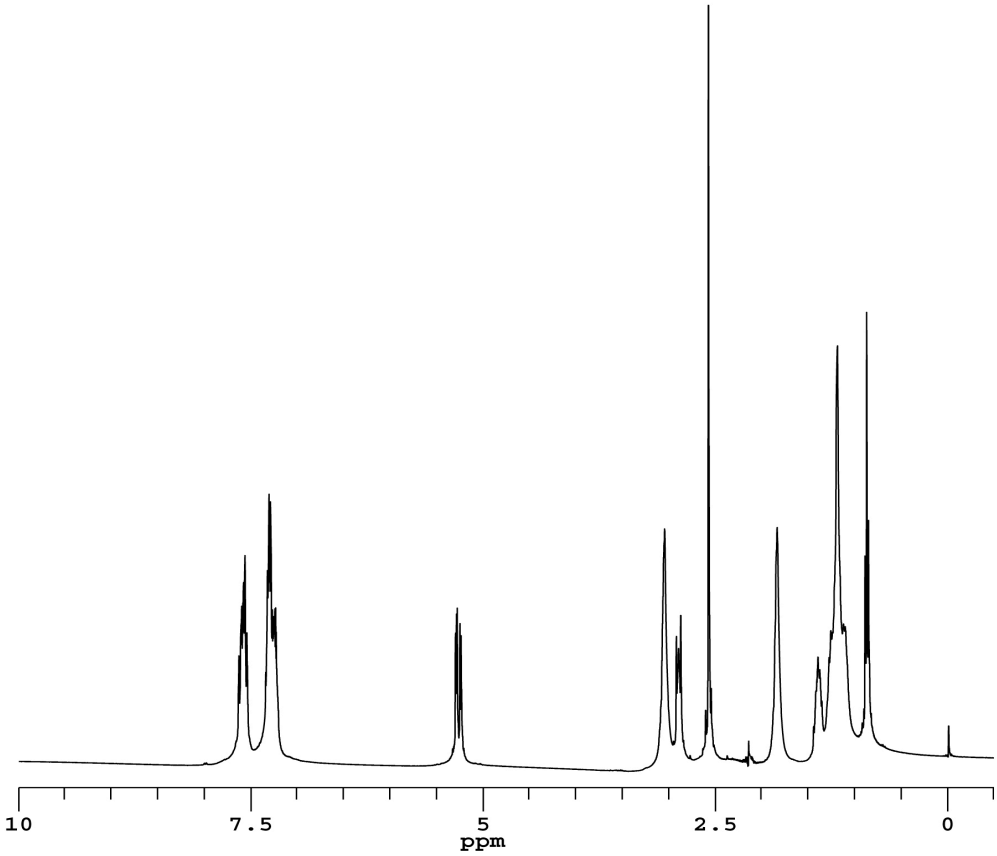

Figure SI-13. 359.92 MHz ^{1}H NMR spectrum of $[C_8C_1Pyrr][BMB]$ in $CDCl_3$.

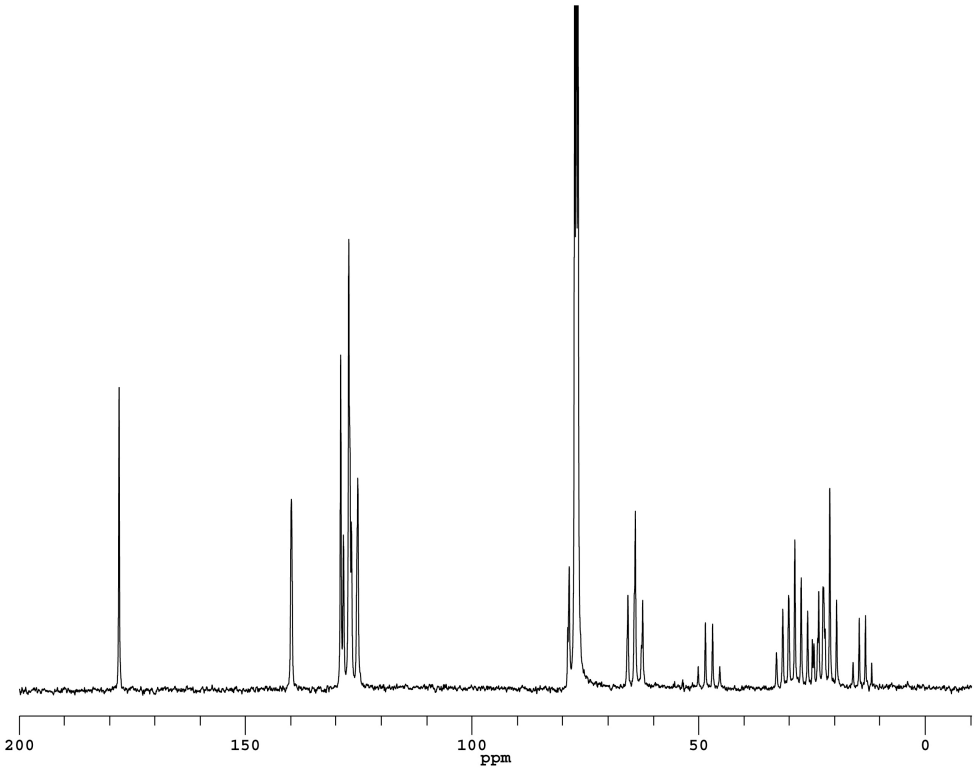

Figure SI-14. 90.506 MHz ^{13}C NMR spectrum of $[C_8C_1Pyrr][BMB]$ in $CDCl_3$.

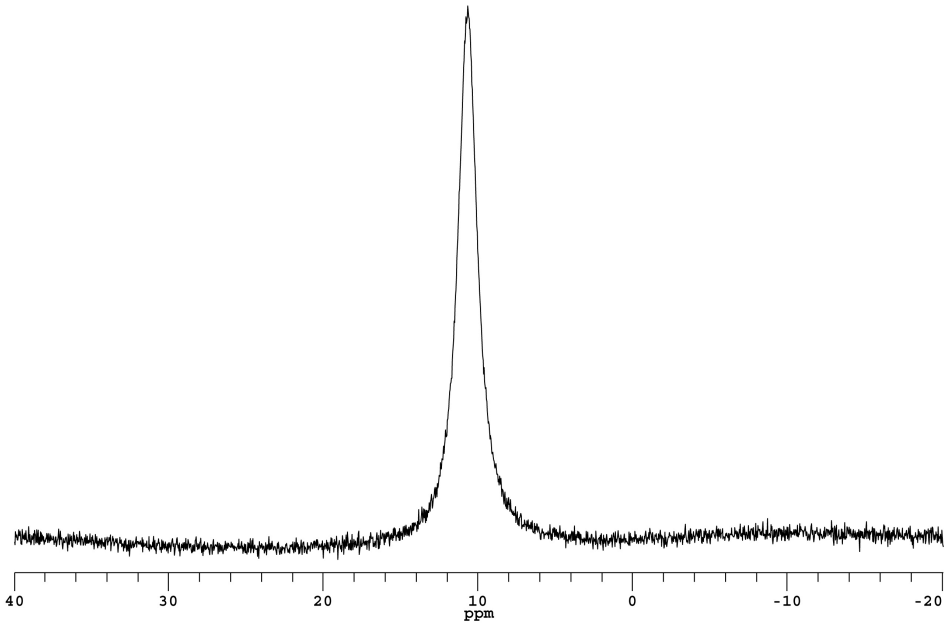

Figure SI-15. 115.48 MHz ^{11}B NMR spectrum of $[C_8C_1Pyrr][BMB]$ in $CDCl_3$.

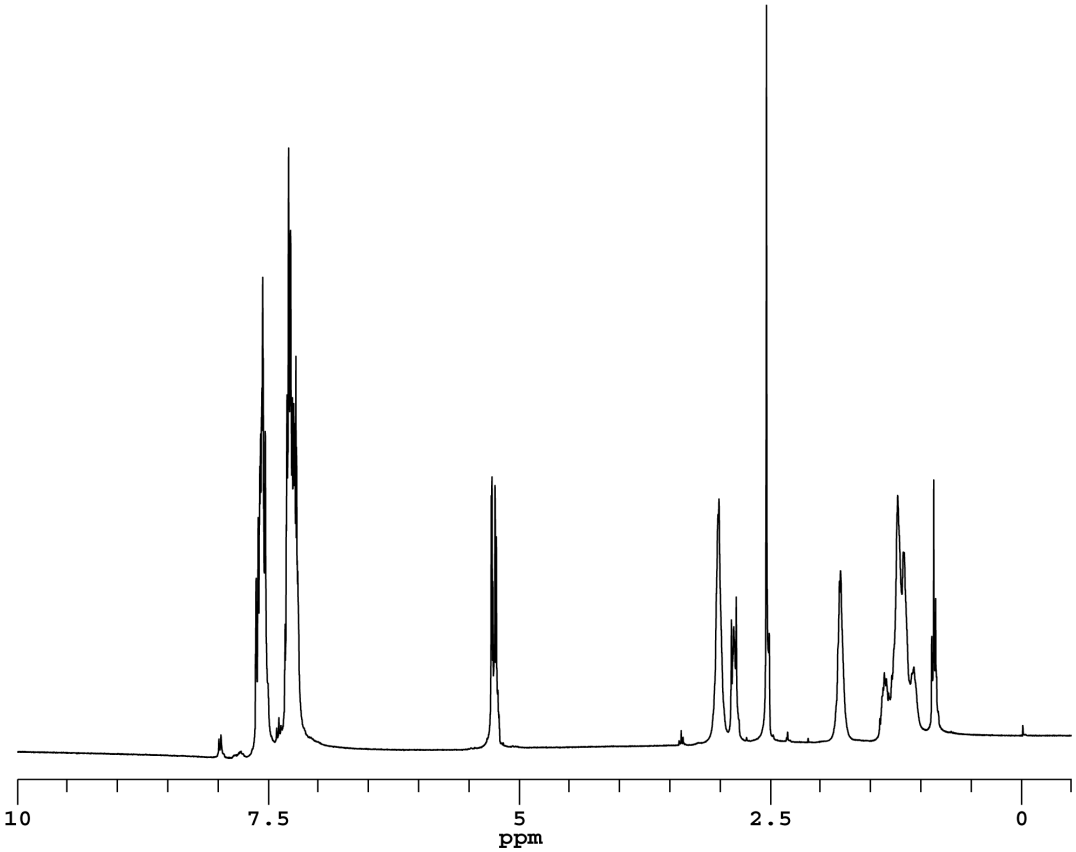

Figure SI-16. 359.92 MHz ^{1}H NMR spectrum of $[C_{10}C_1Pyrr][BMB]$ in $CDCl_3$.

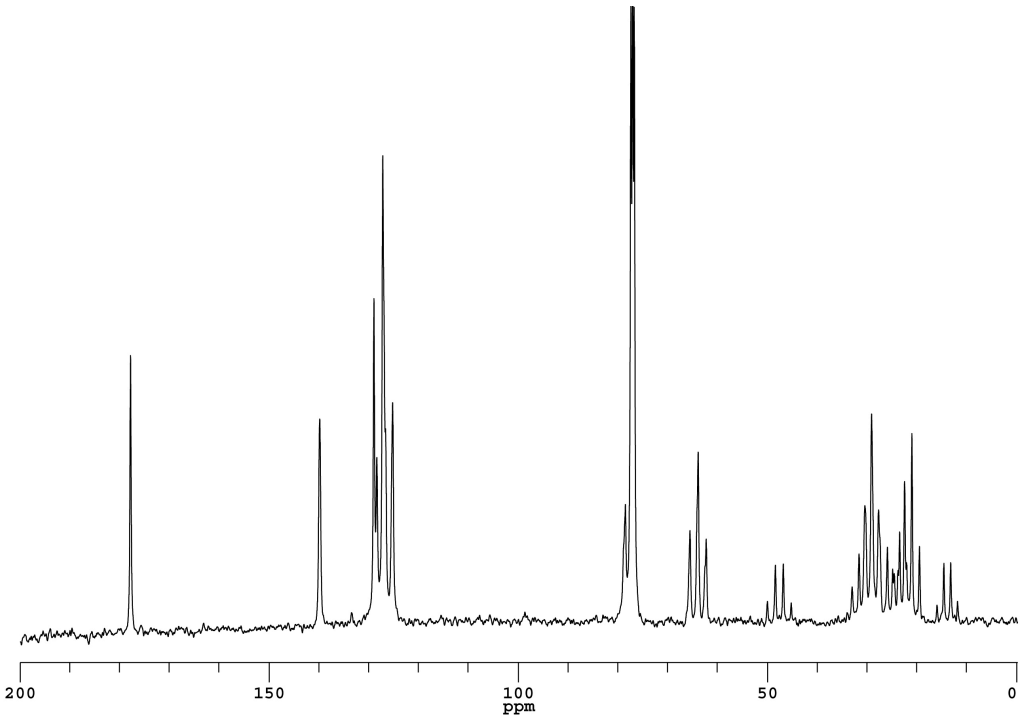

Figure SI-17. 90.506 MHz ^{13}C NMR spectrum of $[C_{10}C_1Pyrr][BMB]$ in $CDCl_3$.

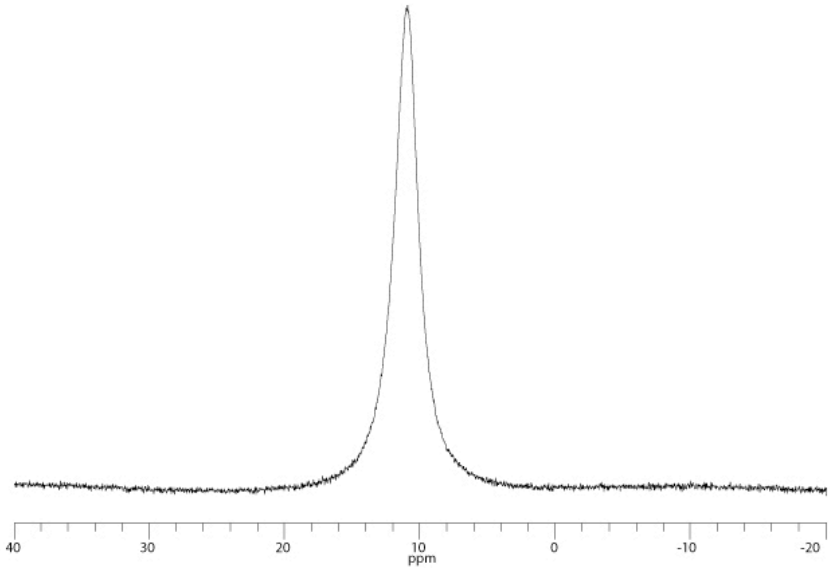

Figure SI-18. 115.48 MHz ^{11}B NMR spectrum of $[C_{10}C_1Pyrr][BMB]$ in $CDCl_3$.

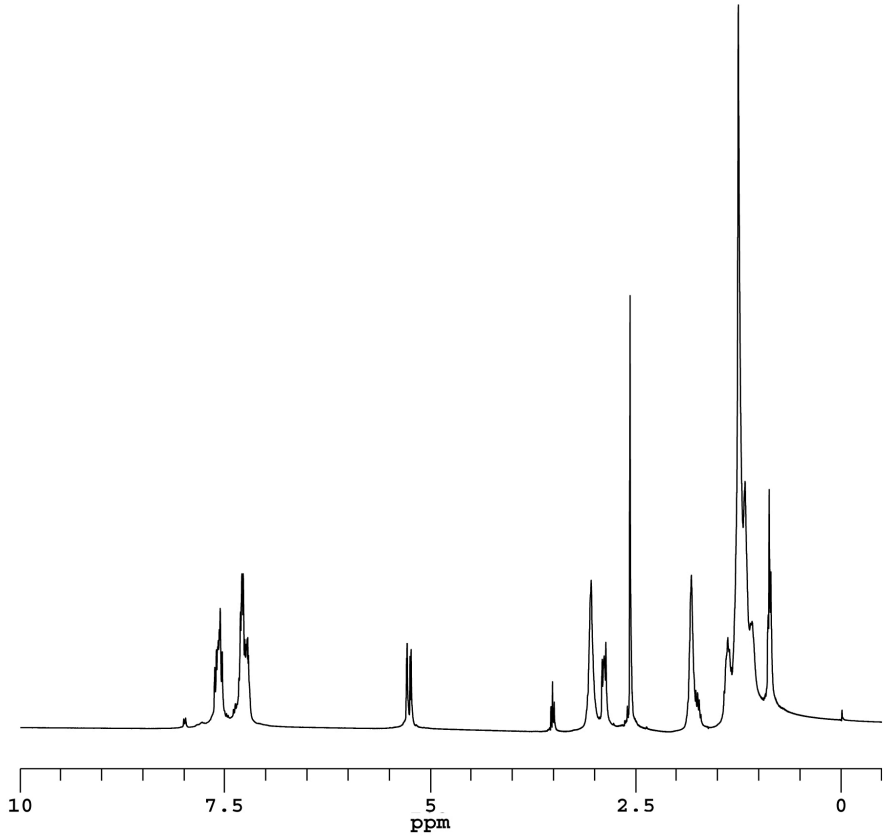

Figure SI-19. 359.92 MHz ^{1}H NMR spectrum of $[C_{12}C_1Pyrr][BMB]$ in $CDCl_3$.

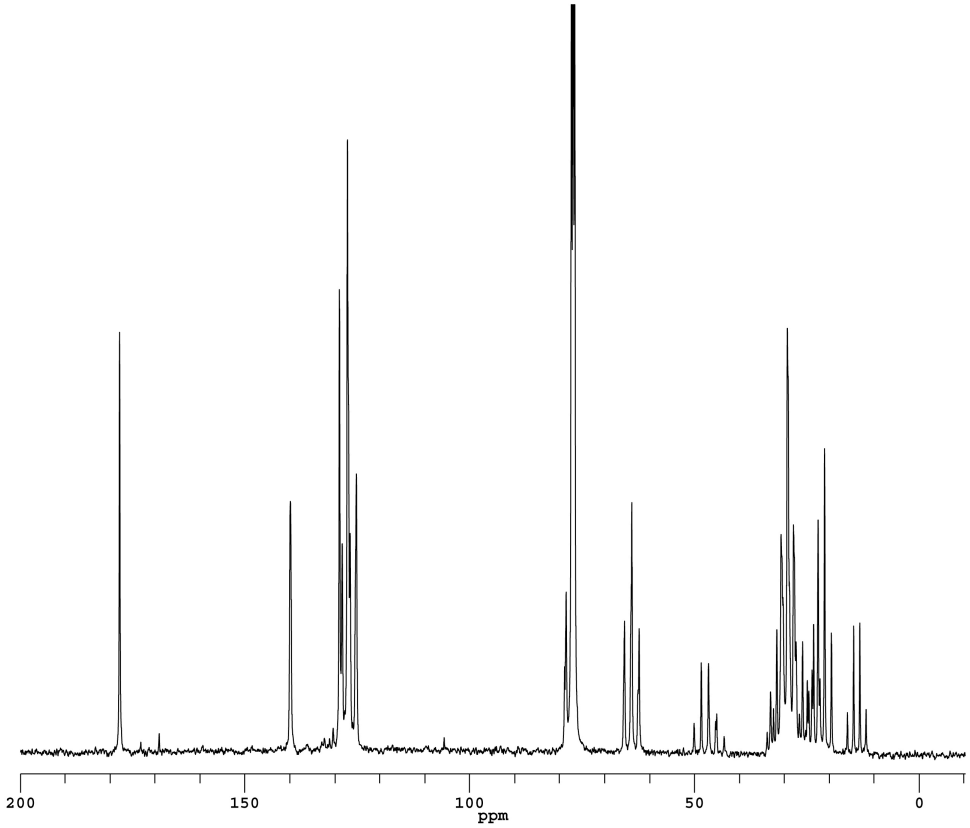

Figure SI-20. 90.506 MHz ^{13}C NMR spectrum of $[C_{12}C_1Pyrr][BMB]$ in $CDCl_3$.

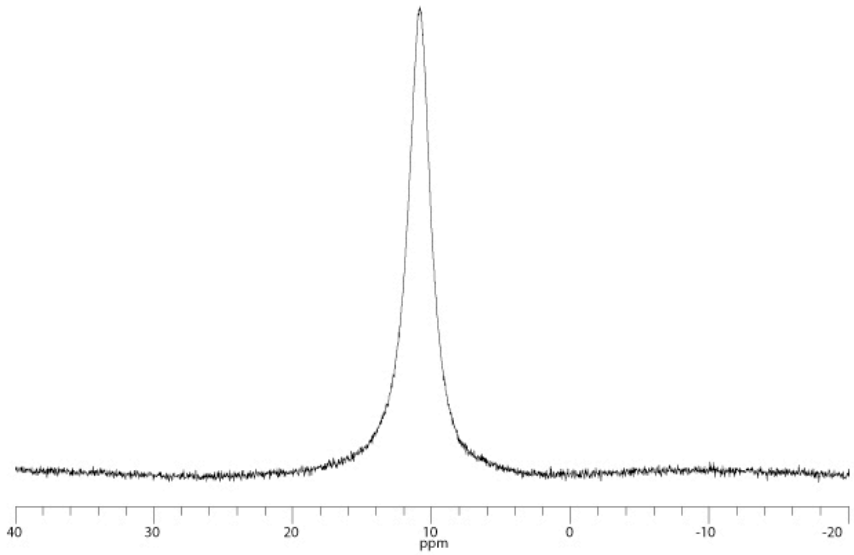

Figure SI-21. 115.48 MHz ^{11}B NMR spectrum of $[C_{12}C_1Pyrr][BMB]$ in $CDCl_3$.

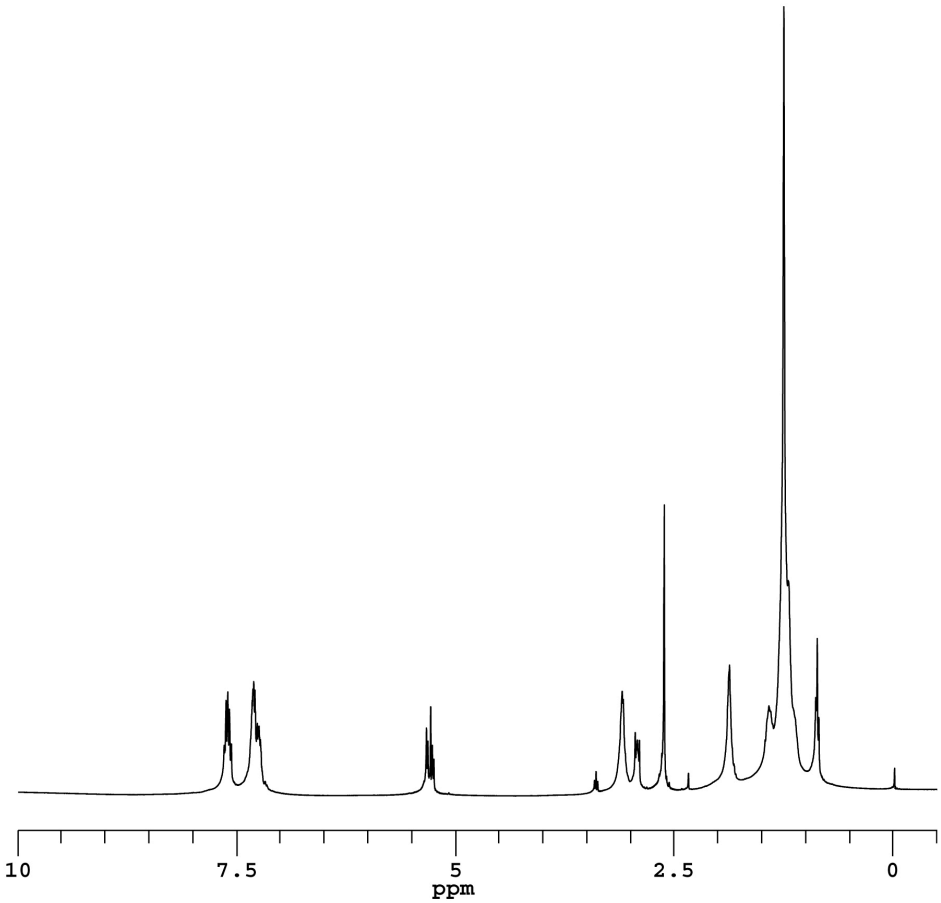

Figure SI-22. 359.92 MHz ^{1}H NMR spectrum of $[C_{14}C_1Pyrr][BMB]$ in $CDCl_3$.

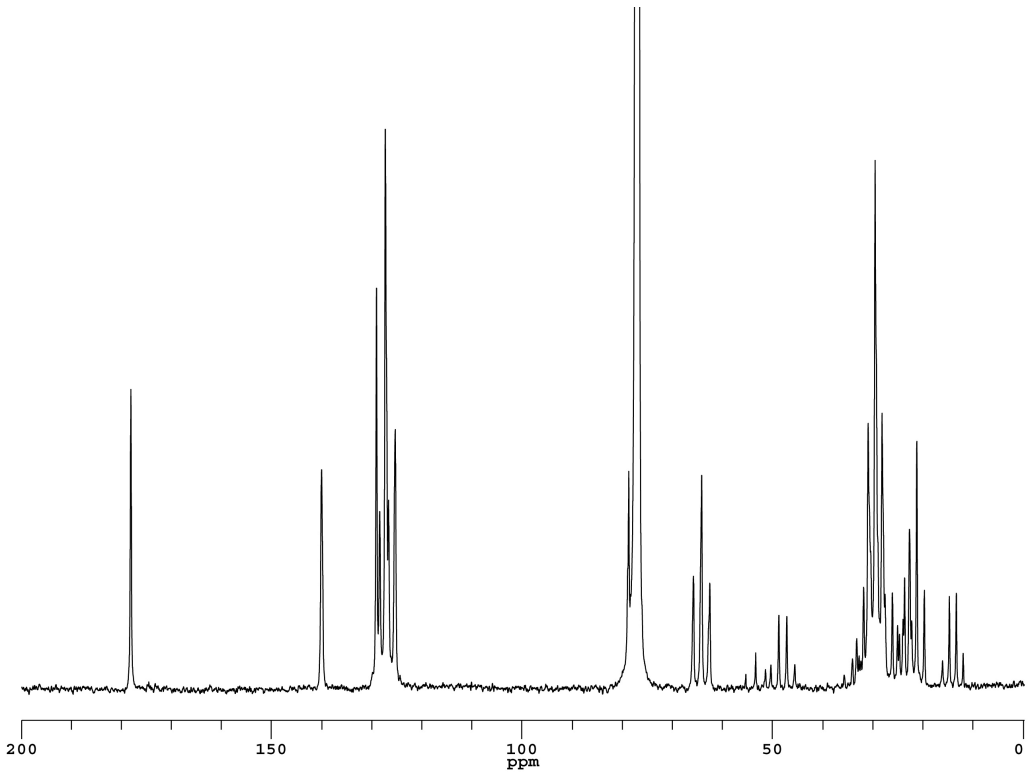

Figure SI-23. 90.506 MHz ^{13}C NMR spectrum of $[C_{14}C_1Pyrr][BMB]$ in $CDCl_3$.

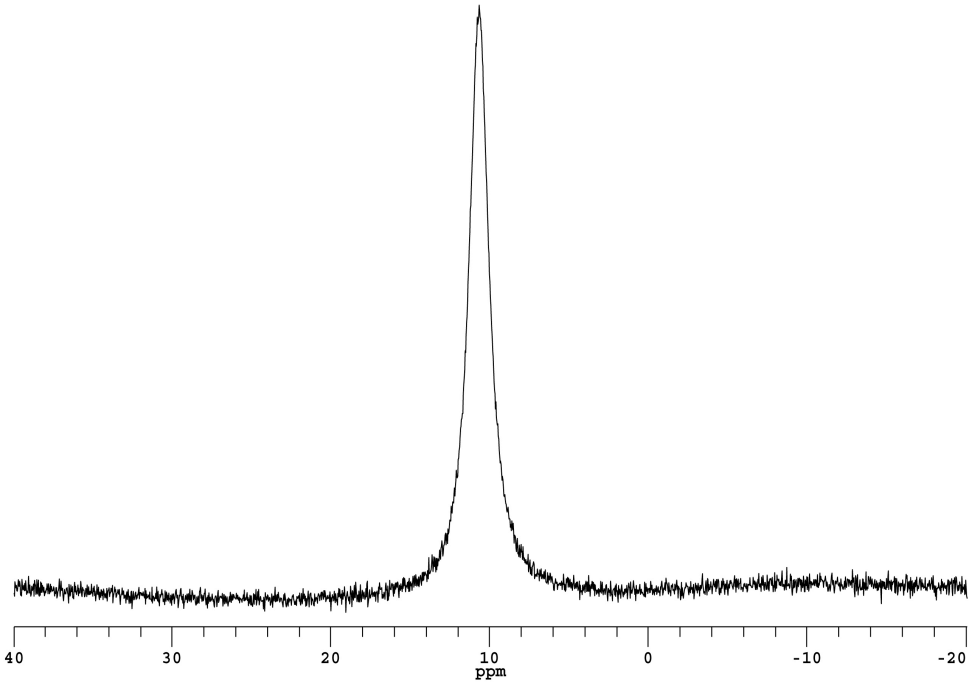

Figure SI-24. 115.48 MHz ^{11}B NMR spectrum of $[C_{14}C_1Pyrr][BMB]$ in $CDCl_3$.

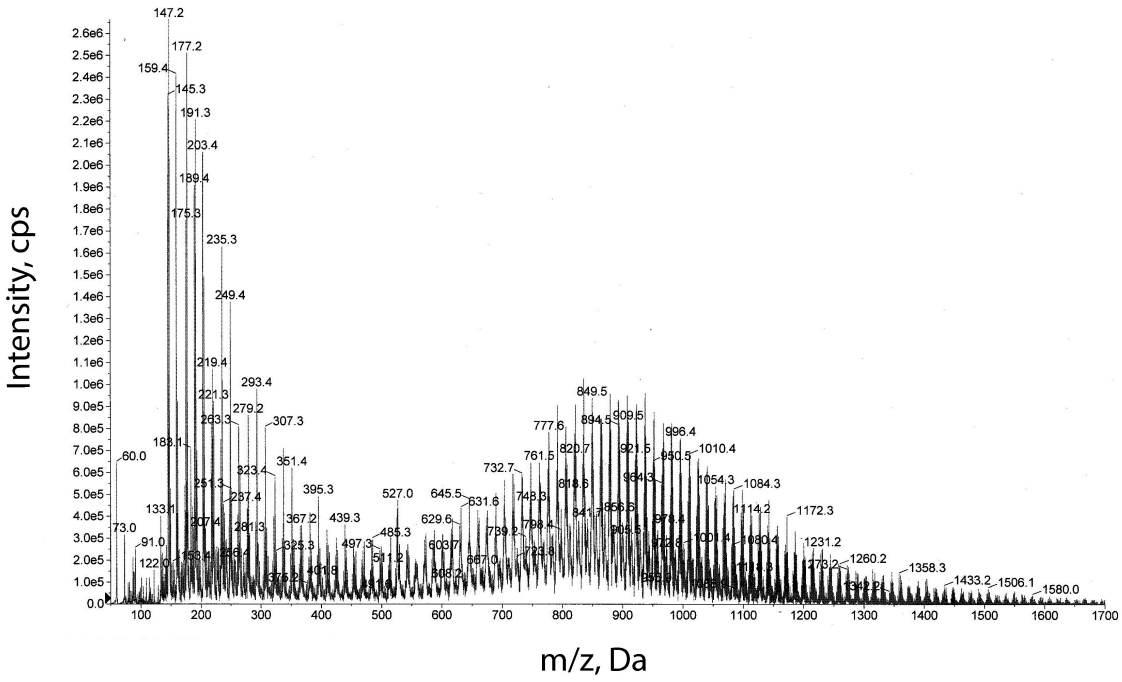

Figure SI-25. Mass spectrum of PEG

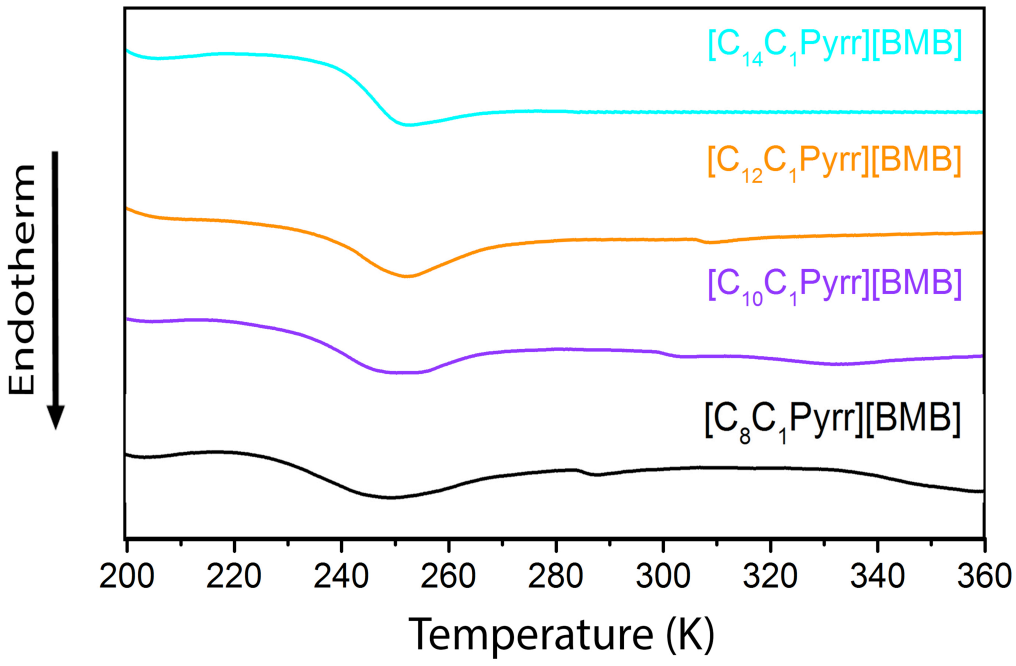

Figure SI-26. DSC thermograms of selected *N*-alkyl-*N*-methylpyrrolidinium bis(mandelato)borate hf-BILs.

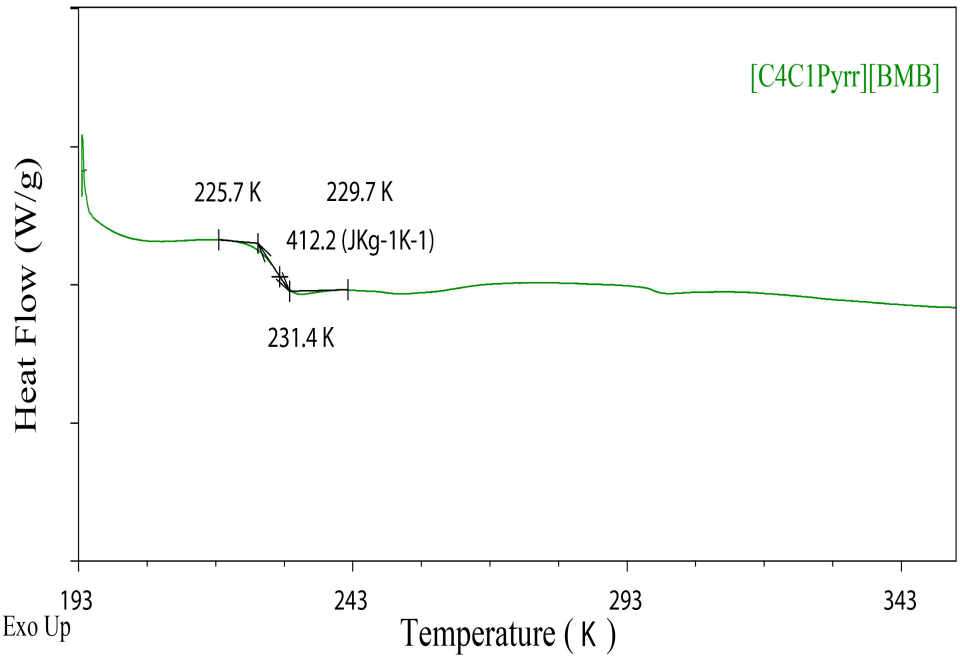

Figure SI-27. A representative labelled DSC thermogram for $[C_4C_1Pyrr][BMB]$ hf-BIL showing T_g and C_p values.

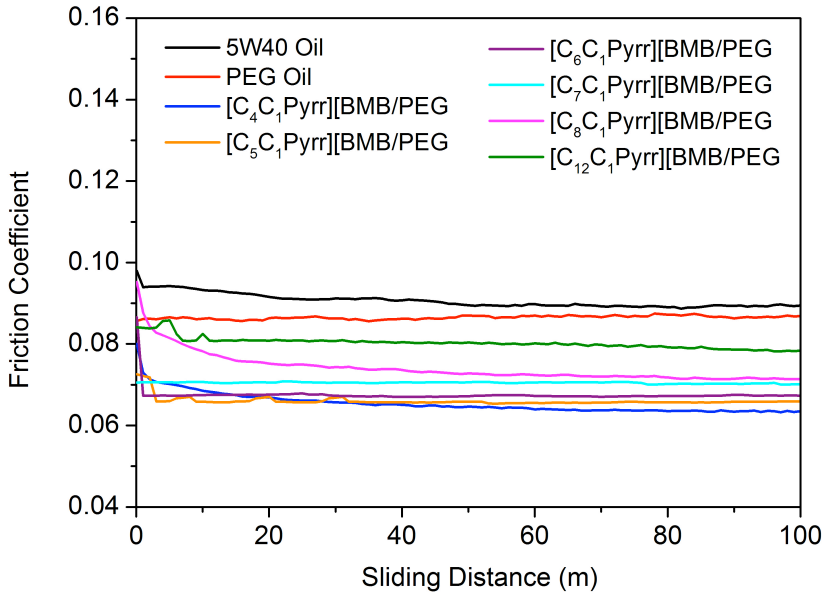

Figure SI-28. Friction coefficient as a function of the sliding distance for steel discs lubricated with 5W40 oil, PEG and 3 wt% of the hf-BILs as additives in PEG. Measurements were performed at 15 N load and 0.2 m/s sliding speed at room temperature.

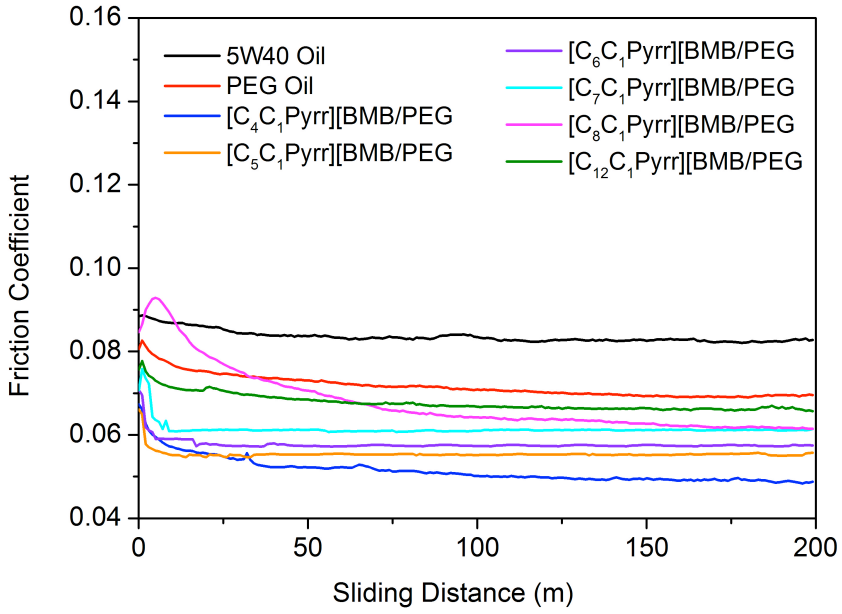

Figure SI-29. Friction coefficient as a function of the sliding distance for steel discs lubricated with 5W40 oil, PEG and 3 wt% of the hf-BILs as additives in PEG. Measurements were performed at 15 N load and 0.2 m/s sliding speed at room temperature.

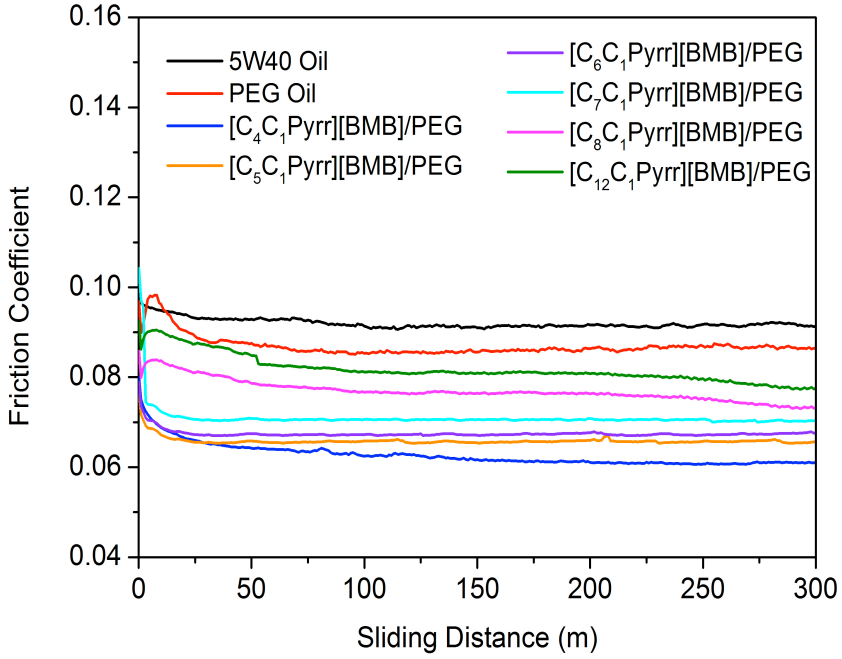

Figure SI-30. Friction coefficient as a function of the sliding distance for steel discs lubricated with 5W40 oil, PEG and 3 wt% of the hf-BILs as additives in PEG. Measurements were performed at 15 N load and 0.2 m/s sliding speed at room temperature.

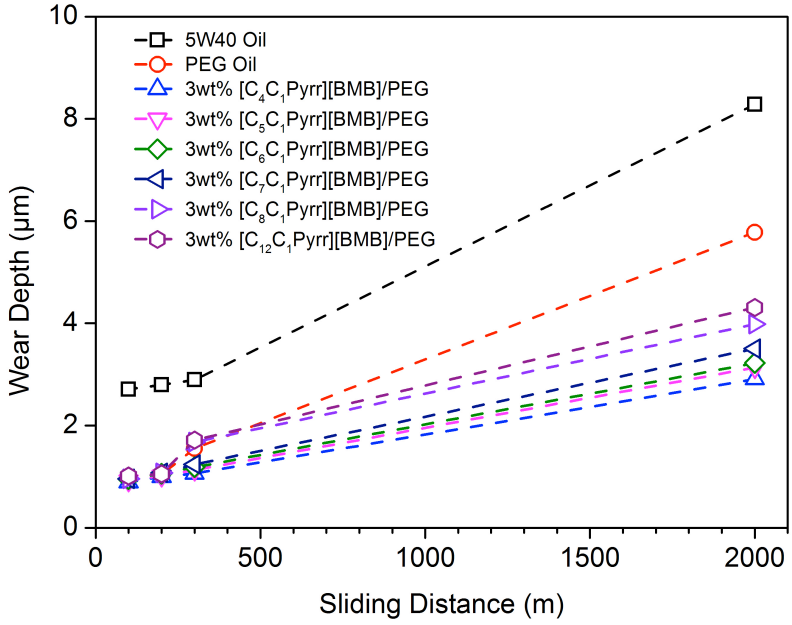

Figure SI-31. Wear depth as a function of sliding distance. Steel-steel contacts tested at room temperature, 15N load, sliding speed of 0.2 m/s.

Table SI-1. Water, sodium and halogen content in hf-BILs

hf-BIL	Water (wt%) ± SD	Sodium (wt%)	Halogen (wt%)	
			Cl	Br
$[C_4C_1Pyrr][BMB]$	0.082 ± 0.002	0.0198	0.0291	0.1784
$[C_5C_1Pyrr][BMB]$	0.078 ± 0.003	0.0141	0.1114	0.5213
$[C_6C_1Pyrr][BMB]$	0.090 ± 0.003	0.0254	0.0951	0.1829
$[C_7C_1Pyrr][BMB]$	0.065 ± 0.007	0.0068	0.0360	0.1024
$[C_8C_1Pyrr][BMB]$	0.109 ± 0.005	0.0135	0.0870	0.0629
$[C_{10}C_1Pyrr][BMB]$	0.075 ± 0.003	0.0068	0.0697	0.3077
$[C_{12}C_1Pyrr][BMB]$	0.038 ± 0.003	0.0134	0.3424	0.0244
$[C_{14}C_1Pyrr][BMB]$	0.035 ± 0.007	0.0114	0.0376	1.0710

Table SI-2. Composition, hardness and surface roughness of the contact surfaces.

Elemental composition (wt%)	AISI 52100 Steel
C	0.95-1.05
Si	0.15-0.35
Mn	0.25-0.45
Cr	1.30-1.65
Mo	0.1 max
S	0.025 max
P	0.025 max
Others	0.15 max
Fe	Balance
Hardness (HRC)	67 (ball) 60 (disk)
Ra (μm)	0.05 max (ball) 0.03 max (disk)

Table SI-3. Measured densities of *N*-alkyl-*N*-methylpyrrolidinium bis(mandelato)borate hf-BILs.

T (K)	**293**	**303**	**313**	**323**	**333**	**343**	**353**
[C_4C_1Pyrr][BMB]	1.1992	1.1916	1.1854	1.1791	1.1719	1.1656	1.1583
[C_5C_1Pyrr][BMB]	1.1946	1.1876	1.1806	1.1742	1.1663	1.1593	1.1523
[C_6C_1Pyrr][BMB]	1.1840	1.1774	1.1698	1.1629	1.1562	1.1499	1.1429
[C_7C_1Pyrr][BMB]	1.1798	1.1724	1.1656	1.1585	1.1521	1.1452	1.1385
[C_8C_1Pyrr][BMB]	1.1705	1.1641	1.1568	1.1506	1.1443	1.1377	1.1311
[$C_{10}C_1$Pyrr][BMB]	1.1599	1.1524	1.1460	1.1396	1.1326	1.1260	1.1206
[$C_{12}C_1$Pyrr][BMB]	1.1504	1.1436	1.1367	1.1299	1.1235	1.1173	1.1112
[$C_{14}C_1$Pyrr][BMB]	1.1398	1.1342	1.1284	1.1222	1.1164	1.1098	1.1030

Wear coefficient calculation:

The wear coefficient was calculated using the formula below:

$$\textit{Wear Coefficient} = \textit{Wear Volume} / (\textit{Load} \times \textit{Sliding Distance})$$

References

1. http://www.mikrokemi.se.
2. http://www.alsglobal.se